

CHAPTER 6

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN ADSORPTIVE MEDIA PROCESSES FOR THE REMOVAL OF ARSENIC

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Appendix A Arsenic Speciation Method Developed by Battelle for EPA

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the Environmental Technology Verification (ETV) Technology Specific Test Plan (TSTP) for evaluation of water treatment equipment for arsenic removal utilizing the adsorptive media process. This TSTP is to be used as a guide in the development of Product Specific Test Plan (PSTP) procedures for testing adsorptive media equipment, within the structure provided by, "Protocol for Equipment Verification Testing for Arsenic Removal: Chapter 1, General Requirements." This TSTP is applicable only to granular adsorptive media processes that use a material, such as activated alumina, that attracts arsenic ions to adsorption sites, with or without pH adjustment in fixed or moving packed beds. Powdered adsorptive media may also be effectively utilized in combination with chemicals in Coagulation and Filtration Arsenic Removal Processes. Since performance of powdered adsorptive media is to be included in that equipment category it is not included in this TSTP.

To participate in the equipment verification process for adsorptive media, the equipment manufacturer and its designated Field Testing Organization (FTO) shall employ the procedures and methods described in this TSTP and in the referenced ETV protocol document as guidelines for the development of the PSTP. The procedures shall generally follow those tasks related to verification testing that are outlined herein, with changes and modification made for adaptations to specific equipment. At a minimum, the format of the procedures written in the PSTP for each task should consist of the following sections:

- Introduction;
- Objectives;
- Work Plan;
- Analytical Schedule; and
- Evaluation Criteria.

Each PSTP shall include Tasks 1 through 5. An overview of Tasks 1 through 5 is provided in Section 4.0 of this TSTP.

2.0 INTRODUCTION

This TSTP is applicable to the testing of package and modular water treatment equipment utilizing an adsorptive media process, which may include a pretreatment pH adjustment step. Verification testing shall evaluate performance of the equipment under at least one feed water quality condition. Waters containing naturally occurring arsenic are preferable to synthetic water "spiked" with arsenic. Use of feed water artificially spiked with arsenic, a product of a non-standard method, might provide inaccurate performance data, which will not reflect performance data acquired with use of natural water. Verification tests will be performed during time periods when the source water or feed water quality is appropriate for testing the full range of water quality conditions that need to be evaluated.

Adsorption can be an effective treatment technique for removing arsenic prior to disinfection application. Adsorptive media processes are operated as filters usually containing a 28x48 US

standard mesh size. Typical empty bed contact times (EBCTs) are 5 to 10 minutes. Arsenic removal is typically greater than 99 percent at the beginning of adsorptive media vessel operation for EBCTs greater than 5 minutes. Over time, effluent concentrations increase, yielding a characteristic breakthrough curve that is unique to the water source, pretreatment conditions, EBCT, and type of adsorptive media used. Thus, the adsorptive media vessel run time for a given treated water criterion can be determined from the appropriate breakthrough curve. Once effluent criteria are exceeded, the adsorptive media must be regenerated or replaced with new adsorptive media.

This TSTP is not intended to be used for the evaluation of ability of adsorptive media to serve as a particulate matter (turbidity) filter. The TSTP for Coagulation and Filtration should be used in conjunction with this TSTP when verification of particulate matter filtration performance is required.

2.1 Adsorption Process

The adsorption process is the physical attraction of the ion to be adsorbed to the surface of the adsorbent material. The adsorbed ion (adsorbate) gathers on to the surface of the adsorbent. The process is sensitive to the concentration of the adsorbate, the surface area of the adsorbent, the physical characteristics of both the adsorbent and/or the adsorbate, competing ions, time, and flow characteristics of the medium conducting the adsorbate into the treatment bed of adsorbent. In this case, arsenic is the adsorbate.

Arsenic occurs in water in two valence states (As III and As V.) The valence state can be modified by oxidation and reduction processes. The toxicology of arsenic varies depending upon its concentration and valence. Since arsenic valence can change while in aqueous solution, the objective of arsenic removal treatment is to remove all of the arsenic regardless of valence. The higher the arsenic concentration is in the feed water, the higher the adsorptive driving force that results in a higher arsenic capacity of the adsorptive media.

The adsorptive capacity of the treatment media is also a function of the surface area (adsorption sites) and the access to those sites. An adsorptive media's surface area is a function of its porosity. An adsorptive treatment media contains an extensive network of fine (small diameter) pores, which extend throughout the body of a grain of media. The adsorptive attraction force is a function of the pore size, the ion size, the pH and other physical conditions. The arsenic ion requires time to migrate into a pore within the grain of the adsorbent. As the surface area of each adsorbent grain becomes saturated with arsenic ions, the time required for additional adsorption becomes longer.

The adsorptive media is normally in a packed bed and contained in a pressure vessel. The water to be treated flows in one direction through the treatment bed (normally downflow). Gravity flow is feasible; but if pH adjustment is employed, gravity flow is not as effective because in gravity flow the pressure required to retain the CO₂ in solution does not exist. Therefore, the free CO₂ is released resulting in the pH rising to higher than the desired level. As the feed water flows through the adsorptive media, the arsenic ions are adsorbed onto the available adsorption sites. As the adsorption sites are being occupied, the arsenic ion concentration decreases in the

water. As the water flows through the bed, its arsenic concentration decreases until no longer detectable. The water continues to flow through the media until it exits the treatment vessel as treated water. As the feed water continues to flow through the treatment media, the media which first contacts the feed water becomes saturated with arsenic ions. A treatment band then progresses through the treatment bed until breakthrough occurs. At that point, traces of arsenic appear in the treated water. As flow continues, the treatment band progresses through the treatment media until the media is saturated; the arsenic concentration in the treated water is then the same as that in the feed water. Since the arsenic concentration in the treated water is the contaminant of concern, the arsenic concentration must be controlled to the desired level.

There are various methods of sequencing multiple treatment beds (parallel and/or series arrangements) which allow the entire (or almost the entire) adsorptive media capacity to be utilized. When the adsorptive media becomes saturated with arsenic ions, it is removed from service for regeneration or disposal. Normally the economic feasibility of the adsorptive process requires reuse of the treatment media. This is accomplished by means of chemical regeneration requiring adjustment of pH (or other methods) to a level at which adsorptive conditions no longer exist. At those pH levels the adsorptive treatment media desorbs the adsorbate. The arsenic is released and flushed from the adsorptive media as a high concentration arsenic wastewater. Upon completion of regeneration, the pH of the treatment media is to be adjusted back to the treatment pH at which point the media is reused for a subsequent treatment cycle. During regeneration, some adsorptive media may be consumed (attrition); if that occurs, replacement adsorptive media is to be added to the treatment bed. In small treatment systems and/or in treatment systems in which the arsenic concentration in the feed water is not excessively high, economic feasibility might dictate replacement of spent media in lieu of regeneration.

2.2 Adsorbents

The following is a list of adsorbents that may be included in the use of this TSTP. This list is not an all-inclusive list since other types of adsorbent materials are currently being developed.

- Activated alumina;
- Ferric Media; and
- Greensand.

2.3 Capacity

Capacities and performance of different adsorptive media do vary. Some adsorptive media may be capable of regeneration while others may not. Those adsorptive media that have regeneration capability also may vary in performance during subsequent treatment runs. The arsenic removal capacity diminishes until it is determined that adsorptive media replacement is required. Other adsorptive media experience attrition during each regeneration requiring addition of makeup adsorptive media prior to commencement of the next arsenic removal treatment run. The latter type of adsorptive media may not experience reduction of arsenic removal capacity during subsequent treatment runs. The treatment system manufacturer may choose to include verification of the regeneration process in its PSTP.

2.4 Intermittent Operation

In full-scale operation, adsorptive media arsenic removal water treatment systems may operate intermittently. The smaller the system the higher the probability that the operation will experience more frequent starts and stops. The performance of adsorptive treatment media is usually not degraded when operated on an intermittent basis. In fact, the performance of this form of treatment media may exhibit a short period of improved performance during startup after a shutdown of the process. The reason for the improved performance is that arsenic ions adsorbed during continuous operation occupy adsorption sites that are most accessible. During process shutdown, the arsenic ions migrate from the most accessible adsorption sites to less accessible sites located deep in the pores of the media thereby re-exposing the most accessible adsorption sites for reuse. At the time the treatment process restarts, the arsenic removal process exhibits increased capacity for a short period after which time the performance returns to the level occurring at time of treatment process shutdown. The treatment system manufacturer may include optional intermittent operational steps in its PSTP.

Adsorptive media treatment systems experiencing extended shutdowns (several weeks) might require a backwash step to expand the media bed to eliminate performance degradation. Degradation will vary due to channeling, biological activity, cementing of media, and other types of process fouling for which potential exists due to characteristics of either the adsorptive media or the water to be treated.

3.0 GENERAL APPROACH

This TSTP is directed to the completion of two main tasks: System Integrity Verification Testing and Adsorption Capacity Verification Testing. An optional third task applies to media that can be regenerated: Regeneration Verification Testing.

System Integrity Verification Testing is a two-week field operation of the equipment with monitoring to ensure the system is functional and to identify any major systemic problems such as channeling, insufficient media, excessive headloss buildup, etc. This TSTP includes sampling and monitoring requirements for System Integrity Verification Testing. Adsorption Capacity Verification Testing is intended to evaluate the capability of adsorptive media at a set contact time to remove arsenic to the level established by the manufacturer. For media that is regenerated, this task includes a mandatory regeneration of the media and a short post regeneration monitoring period. An optional Regeneration Verification Testing task is intended to evaluate the performance of the media through at least two regeneration cycles. This optional task can be important in determining the impact on treatment efficiency, as some media may show a decrease in performance after one or more regeneration cycles.

The manufacturer's statement of performance capabilities is used to establish data quality objectives (DQOs) to develop the experimental design of the verification test. The broader the performance capabilities, the more comprehensive the PSTP must be to achieve the DQOs. An example of a performance capability statement that may be included in an PSTP is: "This system, when operated at an adsorption media EBCT of 5 minutes or more, is capable of

achieving an effluent arsenic concentration of 10 parts per billion or less for at least 10,000 bed volumes for influent arsenic concentrations up to 0.12 mg/L (species of arsenic must be indicated if applicable, i.e., arsenic III or arsenic V).”

Testing shall be conducted by an FTO that is qualified by NSF International (NSF) and is selected by the manufacturer. Water quality analytical work to be completed as part of this TSTP shall be contracted with a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA.

The influent water quality chosen for Adsorption Capacity Verification Testing should be appropriate for the performance capabilities outlined by the manufacturer. Multiple capabilities based on the ability of a system to treat a variety of influent water quality conditions must be supported by Adsorption Capacity Verification Testing performed under conditions representative of this range of water quality. Adsorption Capacity Verification Testing must be conducted at least once using the equipment. Additional testing may be performed to demonstrate performance capabilities that include higher or lower influent arsenic concentrations.

The manufacturer shall stipulate which pretreatment processes are necessary prior to the adsorptive media. The recommended pretreatment processes shall then be employed as pretreatment during equipment verification testing. Adsorptive media performance will be evaluated based on influent water quality, sampled after any pretreatment processes.

4.0 OVERVIEW OF TASKS

The following section provides a brief overview of the tasks included in this adsorptive media TSTP.

4.1 Task 1: System Integrity Verification Testing

The objectives of this task are to demonstrate that the equipment is (1) able to initially produce a finished water as described in the manufacturer’s performance objectives, and (2) able to reliably operate under field conditions. The equipment is operated, monitored, and sampled for approximately two weeks.

4.2 Task 2: Adsorption Capacity and Regeneration Verification Testing

4.2.1 Task 2A: Adsorption Capacity Verification Testing

The objective of this task is to evaluate the ability of the adsorptive media equipment to remove arsenic, based upon the water quality performance capabilities specified by the manufacturer. The performance of the adsorptive media package is a function of the type of adsorptive media used and the feed water quality. Task 2A, Adsorption Capacity Verification Testing, must be performed at least once using the equipment and may be repeated, as necessary, using different water sources to verify the ability of the equipment

to meet multiple treated water quality performance capabilities stated by the manufacturer. Adsorptive media influent and effluent analyses performed include arsenic, pH and other ions that are identified in the feed water. The duration of testing will depend on treatment performance capabilities stated by the manufacturer. If the media is normally regenerated, it must be regenerated after reaching capacity. For media requiring regeneration, one regeneration cycle will be monitored and a post-regeneration monitoring period will be included for this task.

4.2.2 Task 2B: Regeneration Verification Testing (Optional)

This task applies only to media that is regenerated as part of the normal treatment process and is an optional task. The objective of this task is to evaluate the impact of the regeneration process on the ability of the media to meet the water quality performance capabilities specified by the manufacturer. Regeneration of media is specific to the media type and the regeneration process. Some media experience a decrease in performance or capacity after one or more regeneration steps. If this optional task is performed, a minimum of two full regeneration cycles must be monitored, including a post-regeneration monitoring period after the second regeneration cycle. Task 2B can be expected to be twice as long as Task 2A, with the first regenerative cycle being included as part of Task 2A. Adsorptive media influent and effluent analyses performed include arsenic, pH and other ions that are identified in the feed water and any specific ions that may be important to the regeneration process. The duration of testing will depend on treatment performance capabilities supplied by the manufacturer and the volume of water that can be treated between regeneration cycles.

It may be possible to perform this verification task using existing data and experience from a similar site. Given the long run times between regenerations for some media, the ETV Program will consider the use of well-documented data and operating records from installations that have years of information. The source water will need to be similar and the treatment system must use the same media and treatment process. Acceptance of existing data will be on a case-by-case basis. The use of existing data may be reviewed by the ETV Program and included in ETV verification reports and statements as separate and distinct from verified data.

4.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance

The objective of this task is to observe, measure, and document the operating conditions throughout the verification test. During each day of verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. The volumetric flow rate through adsorptive media vessels is a critical parameter, and shall be frequently monitored, recorded, and adjusted if necessary. Adsorptive media performance is affected by the EBCT, which is a function of the volumetric flow rate through the adsorptive media vessel. If media regeneration is applicable, the volume and flow rate of regenerative fluids shall be monitored and recorded. Operating conditions immediately following the completion of the regeneration process shall be monitored and recorded to

determine if any changes have occurred within the treatment system.

4.4 Task 4: Data Management

This task will establish effective field protocol for data management at the field operations site and for data transmission between the FTO and NSF.

4.5 Task 5: Quality Assurance/Quality Control

The objective of this task is to ensure accurate measurement of operational and water quality parameters during verification testing.

5.0 TESTING PERIODS

Task 1, System Integrity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5 in a two-week period, not including mobilization and start-up. When verifying package plants or module components for small systems and very small systems, the equipment shall be operated for a minimum of two hours or longer depending on the actual application, and then the flow to the equipment shall be stopped and operations resumed the next day. After the completion of Task 1, subsequent testing may use the normal intermittent or continuous flow pattern that is typical for the test site. Task 2A, Adsorption Capacity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5. The duration of Task 2A is dependent on the volume of water required (as specified in the manufacturer's statement of performance capabilities), the flow rate processed through the system, the run time, the source water quality, and other factors that may affect media capacity. Task 2B is designed to be carried out in conjunction with Tasks 3 through 5. This task will include a minimum of two full regeneration cycles, so the duration of the test will be dependent on the same factors as Task 2A. Task 2B can be expected to be twice as long as Task 2A, with the first regenerative cycle being included as part of Task 2A.

6.0 DEFINITIONS

Definitions that may apply to adsorptive media processes include:

- 6.1 Adsorb:** To adhere on a surface in a condensed layer.
- 6.2 Adsorptive Media, Granular:** Particles retained on a 100 mesh screen that have ability to adsorb. During the treatment process, these materials are contained in a treatment vessel.
- 6.3 Adsorptive Media, Powdered:** Particles that pass through a 100 mesh screen that have ability to adsorb. During the treatment process, these particles are added into and mixed with the water to be treated. The particles are removed from the treated water by sedimentation and/or filtration.

- 6.4 Bed Volume:** The volume of adsorptive media including voids between particles contained in a treatment vessel.
- 6.5 Breakthrough:** The point in adsorptive media run time when the effluent arsenic concentration reaches a predetermined value, such as the detection limit, the maximum contaminant level (MCL), some fraction of the MCL, etc.
- 6.6 Desorb:** To remove an adsorbate from an adsorptive media surface.
- 6.7 Empty Bed Contact Time (EBCT):** The volume of the media divided by the flow rate. For example, the time (EBCT) required for feed water flowing at 150 gpm through an adsorptive treatment media volume of 100 ft³ (750 gallons) is 5 minutes.
- 6.8 Filtrate:** Liquid that has passed through a filter.
- 6.9 Ground Water:** Water located below grade, which is not under the influence of surface water. The source of water in wells and springs.
- 6.10 Regenerate:** To renew or restore treatment capacity to adsorptive media.
- 6.11 Supernatant:** Liquid above a sludge layer.
- 6.12 Surface Water:** All water that is open to the atmosphere and subject to surface runoff. For purpose of this document, surface water includes lakes, reservoirs, canals, rivers, streams, and ground water under the influence of surface water.
- 6.13 Treatment:** To subject to some agent or action to bring about a particular result.
- 6.14 Treatment Band:** The portion of a bed of adsorptive media in which treatment takes place.
- 6.15 Treatment Bed:** The space occupied by the adsorptive media.

7.0 TASK 1: SYSTEM INTEGRITY VERIFICATION TESTING

7.1 Introduction

This task will evaluate the short-term ability of the equipment to produce water of acceptable quality. This task is not designed to evaluate the long-term ability of the equipment to remove arsenic.

7.2 Experimental Objectives

The objectives of this task are to demonstrate that the equipment is (1) able to produce a treated

water within performance capabilities, and (2) able to reliably operate under field conditions.

7.3 Work Plan

The manufacturer and its designated FTO shall specify in the PSTP the operating conditions to be evaluated during verification testing and shall supply written procedures on the operation and maintenance of the treatment system. To complete the System Integrity Test, for applications where the treatment system is expected to operate continuously, the equipment shall be operated continuously for a minimum of 320 hours (13 full days plus one 8-hour work shift). For applications where the treatment system is expected to operate intermittently, such as for very small systems, the equipment shall be operated for a minimum of two hours continuously each day throughout the 13 full days plus one 8-hour work shift period. For adsorptive media vessels operated as post-filter adsorbers, the media filters on-line upstream of the adsorptive media vessels shall be operated from start-up until turbidity breakthrough or terminal head loss is attained, at which time the media filters shall be backwashed and operation shall resume.

System Integrity Verification Testing shall include at least one backwashing event, as determined by turbidity breakthrough or terminal head loss. For adsorptive media filters that are not operated as post-filter adsorbers, but specify that a backwash cycle is part of normal operation, at least one backwashing event at the end of the System Integrity Verification Test shall be included in the test. This backwash shall be performed even if the backwash criteria (volume treated, headloss or pressure drop, etc.) are not experienced or met. Interruptions in the treatment system shall be documented and are allowed only for backwashing events and required equipment maintenance. Since adsorptive media performance is a function of EBCT, which is dependent on the volumetric flow rate, it is critical that verification testing be conducted at a set flow rate that is maintained within 5 percent of the design value.

Water Quality Sample Collection. Water quality data shall be collected at regular intervals as described in the analytical schedule (see Table 1). Additional or more frequent analyses may be stipulated at the discretion of the FTO. Sample collection frequency and protocol shall be defined by the FTO in the PSTP.

The arsenic species (III or V) present in the feed water can have a direct impact on the performance of adsorptive processes. It is important that the distribution of arsenic species be determined as part of the verification test. At a minimum, two samples of source water, collected before or during startup and shakedown, and three samples of the feed water and treated water, collected during the Integrity Test, shall be speciated. More frequent arsenic speciation may be needed depending on the actual distribution of the arsenic species in the feed water, and the importance of the arsenic species (III or V) to the performance of a specific treatment process. If the feed water has only one species of arsenic present, then the minimum frequency may be appropriate. However, if the source water has significant concentrations of both species present, and/or the media performance is dependent on the arsenic species, then more frequent or daily arsenic speciation should be proposed by the FTO to properly monitor the system performance.

Sample collection procedures for intermittent flow systems must ensure that freshly treated water is collected and not water that was stagnant in the bed. For intermittent flow systems, sample

collection should occur during a continuous flow period, after a minimum of 10 bed volumes has passed through the system or after one hour of continuous flow.

In the case of water quality samples to be shipped to the laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory. Acceptable methods for the required analytical procedures are described in Task 5, Quality Assurance/Quality Control. All PSTPs shall include, at a minimum, a table(s) showing all parameters to be analyzed, the analytical methods, the laboratory reporting limits or quantitation limits, sample volume, bottle type, preservation method, and holding time.

7.3.1 Spiked Arsenic (Optional)

If the feed water does not contain the level of arsenic concentration required to verify the manufacturer's performance capabilities, arsenic spiking may be employed. Spiked arsenic may be used in concentrations sufficient to permit the most-stressed operations for the manufacturers' equipment, following the recommended guidelines:

- Arsenic spiking shall begin at start-up of the treatment equipment.
- Arsenic feed solution will be prepared by diluting the arsenic into dilution water that is distilled or deionized and oxidant free.
- To spike arsenic (III), use commercially-prepared arsenic trioxide. (In cold water, at 2°C, the solubility of this chemical is about 1.2 g/100 g water.).
- To spike arsenic (V), use commercially-prepared arsenic pentoxide.
- Feed reservoir for the arsenic spike solution shall be made of chemically inert material (i.e., not reactive or adsorbable to the arsenic).
- The reservoir will be mixed continuously throughout the experiment.
- The arsenic spike solution will be fed using an adjustable rate chemical feed pump.
- Use an in-line static mixer to mix this solution into the feedwater.
- Arsenic samples of at least 250 mL shall be collected in bottles prepared for holding such samples.

If testing with Arsenic (III) is contemplated, manufacturers and FTOs need to be aware of potential difficulties in preventing conversion of As (III) to As (V) as the spiking solution is held in its storage container. Further conversion to the higher valence state could occur during passage of spiked water through the equipment. Manufacturers and FTOs should also be aware that there are professional opinions that are opposed to arsenic spiking for adsorptive media verification testing.

If arsenic (III) is spiked, then speciation tests shall be conducted to verify that the arsenic (III) is being fed to the treatment system. The application test that was developed by Battelle for the EPA shall be employed (see Appendix A). Also, if the adsorptive media to be tested does not efficiently remove Arsenic (III), the speciation test developed by

Battelle shall be employed. Please note when using this method that ultra-pure (optimum) grade sulfuric acid must be used (not reagent grade) to avoid the trace amounts of arsenic that can be present in reagent grade sulfuric acid.

7.4 Analytical Schedule

Operational Data Collection. The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include, at a minimum, system flow rates and head loss or pressure. Operational data monitoring frequencies are described in Table 2. The FTO shall include acceptable values and ranges for all operational parameters monitored. Data organization and recording is important. An example of chemical consumption data recording is illustrated in Table 3.

Water Quality Data Collection. During System Integrity Testing, the adsorptive media feed water quality and adsorptive media treated water quality shall be characterized by analysis of the water quality parameters listed in Table 1. For applications where the treatment system is expected to operate intermittently, such as for very small systems, the samples shall be collected during the minimum two hours of operation (see *Water Quality Sample Collection Section* above). Additional or more frequent analyses may be stipulated at the discretion of the FTO.

The first sampling for each required analyte shall be performed by means of grab samples one day after plant operation start-up, and then by the frequency given in Table 1 or in the PSTP. Although many parameters may be analyzed off-site, pH, temperature, and turbidity must be analyzed on-site.

It is important when selecting the analytical methods for the various parameters that the procedures achieve detection and reporting limits that are appropriate to meet the objectives of the test. As an example, some arsenic test methods can only detect arsenic above 0.010 mg/L. If the performance of the technology is being verified to meet drinking water standards of 0.010 mg/L, and the capacity test is based on a maximum treated water level of 0.010 or 0.012 mg/L, then a method with a detection limit of 0.010 mg/L would not be appropriate or useful. The selection of each test method must consider how the data will be used, the objectives of the PSTP, and the ability of the method to meet the accuracy and precision objectives specified in the PSTP.

The water quality parameters, listed in Table 1, are selected to provide state drinking water regulatory agencies with background data on the quality of the feed water being treated and the quality of the treated water. These data are to be collected to enhance the acceptability of the System Integrity Verification Testing to a wide range of drinking water regulatory agencies.

7.5 Evaluation Criteria and Minimum Reporting Requirements

The results of System Integrity Verification Testing shall be evaluated based on arsenic removal. Time series plots shall be generated describing adsorptive media influent and effluent arsenic.

The System Integrity Verification Testing should demonstrate the initial ability of the adsorptive media to remove arsenic concentration below detectable levels in the treated water. Detectable levels of arsenic or immediate breakthrough of arsenic are indicative of failure of the treatment system, possibly due to hydraulic channeling, insufficient media, very low adsorptive media capacity, or inappropriate adsorptive media design for the water quality tested. Long-term arsenic removal will be evaluated during Task 2A (Adsorption Capacity Verification Testing) and during optional Task 2B (Regeneration Verification Testing).

8.0 TASK 2A: ADSORPTION CAPACITY VERIFICATION TESTING

8.1 Introduction

The purpose of Task 1 System Integrity Verification Testing is to quickly and efficiently test the basic ability of the adsorptive media vessel (1) to initially yield a treated water of acceptable water quality and (2) to reliably operate under field conditions. After Task 1 has been performed, the long-term effectiveness of the treatment system to remove arsenic shall be evaluated by Task 2A Adsorption Capacity Verification Testing. For a tabulation of physical data requirements for the adsorption media being evaluated, see Table 4.

The breakthrough of arsenic for a given water source is characteristic of the treatment system and will depend on design, EBCT, the type of adsorptive media used, and feed water quality. Breakthrough is highly dependent on the concentration and adsorptive characteristics (isotherm) of the arsenic to be treated by the adsorptive media. Since adsorptive media performance is dependent on feed water quality, the manufacturer may have multiple performance capabilities on the arsenic removal ability of the equipment. Adsorption Capacity Verification Testing shall be performed at least once for a system, but may be performed multiple times utilizing different water qualities to verify multiple performance capabilities. To verify multiple performance capabilities, the FTO shall repeat Adsorption Capacity Verification Testing, utilizing multiple water qualities representative of those described in the performance capabilities, as described below in the work plan.

Some adsorptive media require regeneration when the media becomes saturated with arsenic or other ions, and removal efficiency declines (See discussion in Section 2.1 and 2.4). It is important to assess the regeneration process and its impact on media performance following the regeneration step. Some regeneration processes can cause reduced system performance, as compared to fresh media. Therefore, Task 2A shall include an evaluation of the regeneration process (minimum of one regeneration of the media), and a short post-regeneration monitoring period to assess system performance. A more complete evaluation of the regeneration process and possible impacts on performance is incorporated into optional Task 2B, if the manufacturer chooses to verify the long-term effects of regeneration.

8.2 Experimental Objective

The objective of this task is to evaluate the ability of the adsorptive media employed in the treatment system to demonstrate the water quality performance capabilities specified by the

manufacturer.

The FTO shall identify in the PSTP the treated water quality objectives to be achieved in the statement of performance capabilities of the equipment to be demonstrated during verification testing. The statement of performance capabilities prepared by the manufacturer shall indicate the range of water quality under which the equipment can be challenged, while successfully treating the adsorptive media feed water. One example of a statement of water treatment performance capabilities is provided below:

“This system, when operated at an adsorption media EBCT of 5 minutes or more, is capable of achieving an effluent arsenic concentration less than 10 parts per billion for at least 10,000 bed volumes for influent arsenic concentrations up to 0.12 mg/L (species of arsenic must be indicated if applicable, i.e., arsenic III or arsenic V).”

8.3 Work Plan

Task 2A, Adsorption Capacity Verification Testing, may begin simultaneously with Task 1, System Integrity Verification Testing. Subsequent sessions of Task 2A, Adsorption Capacity Verification Testing, will not require Task 1, System Integrity Verification Testing. The manufacturer shall estimate or specify to the FTO the run time criteria for each Adsorption Capacity Verification Testing period and shall supply written procedures on the operating conditions and maintenance of the treatment system. Run time criteria can be based on treated water quality conditions, or expected capacity of the media. For example, the manufacturer may specify that the equipment be operated until the treated arsenic concentration reaches 0.010 mg/L, or the current MCL. In this example, the manufacturer shall provide the FTO with an estimated volume of water or bed volumes that are expected to be processed before the treated water concentration rises to the target level or slightly above the target level. These estimates are usually based on the known capacity and characteristics of the media, and the concentration of arsenic in the feed water. The manufacturer and FTO will use this information in conjunction with the flow rates that will be used at the site and historical arsenic concentrations at the site to estimate the run time to reach the capacity or manufacturer's performance capabilities. Alternatively, the manufacturer may specify a maximum run time, after which the media needs to be changed or regenerated.

The Adsorption Capacity Verification Testing shall be run for a minimum of sixty (60) days (this includes Tasks 1 and 2A). A combination of treated water quality and maximum run time criteria may also be utilized. The selection of a specified maximum run time should be carefully considered, as the use of a specified run time may result in significantly underestimating (or not verifying) the capacity of a media. If the specified run time option is selected, then the verification test will only be conducted for that specified time, and the test will be either terminated or regeneration will occur (if appropriate), whether or not the media has reached capacity. A specified run time that is short could result in a significant cost disadvantage for a system being compared to similar systems with longer service life between media change out or regeneration. The run time criteria chosen should reflect the specified treatment capability of the system, based on the adsorptive media feed water quality.

Water sources must be chosen carefully so that water qualities are representative of that on which the manufacturer's performance capabilities are based. The arsenic concentration in the feed water should be in the same range as the concentration used to develop the performance capabilities statement. This ensures that Adsorption Capacity Verification Testing adequately tests the equipment's ability to meet manufacturer's performance capabilities for a given water quality. Multiple Adsorption Capacity Verification Testing periods may be necessary to provide verification testing on multiple treatment capabilities. For example, multiple Adsorption Capacity Verification Testing runs may be needed to verify water treatment capabilities if the performance capabilities are stated to cover a wide concentration range, such as 0.02 to 0.20 mg/L. If the feed water does not contain the level of arsenic concentration required to verify the manufacturer's removal capability, arsenic spiking may be employed (refer to procedures outlined in Section 7.3.1).

Media requiring regeneration shall be regenerated at least once at the end of the Adsorption Capacity Verification Test. The manufacturer's recommended procedures shall be followed for regeneration of the media. The FTO shall provide the operating procedures that will be used for regeneration of the media, including specifying the chemicals, solution concentrations, and other pertinent information for regeneration. At the completion of media regeneration, the system shall be placed back to normal service and monitoring shall continue for a minimum of four weeks for comparison to the initial performance data obtained using fresh media.

Any residuals produced during in-place regeneration of the adsorptive media shall be fully characterized and documented with respect to quantity and composition. The information from this residuals characterization task shall be used to determine the efficiency of regeneration. For example, if a low pH solution is used to remove arsenic from the media, this solution shall be monitored for arsenic content and other ions of interest. If a rinsing solution is used, then this liquid will also be measured for arsenic concentration and other ions of interest. A mass balance approach shall be used to determine whether all the arsenic was removed during the regeneration process. The regeneration efficiency and the adsorbent usage rate shall be reported.

Water Quality Sample Collection. Water quality data shall be collected at regular intervals as described in the analytical schedule (see Table 5) and as described below. Additional or more frequent analyses may be stipulated at the discretion of the FTO. Sample collection frequency and protocol shall be defined by the FTO in the PSTP.

The sample collection schedule will be dependent upon the run time estimate developed for the specific media. The FTO will develop a sample collection and analytical schedule that collects sufficient data to define the breakthrough or capacity curve. The actual total number of samples collected for this task will be dependent on the run time estimate and the actual length of time to reach the capacity of the media. Frequent sampling (e.g. daily or 3 times per week) could result in 100 samples or more being collected, if the run time is several months. This large number of samples may not be cost effective. It is important, however, that several sets of data are available near the breakthrough point to properly define the capacity of the media, and that regular monitoring occurs throughout the test period. Table 5 provides minimum sampling intervals that should be considered by the FTO.

In the case of water quality samples to be shipped to the laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory. Acceptable methods for the required analytical procedures are described in Task 5, Quality Assurance/Quality Control. All PSTPs shall include, at a minimum, a table(s) showing the parameters to be analyzed, analytical method, the laboratory reporting limit or quantitation limit, sample volume, bottle type, preservation method, and holding time.

The FTO shall develop an overall sampling plan and schedule for all parameters based on the guidance in this document, the estimated length of the test based on the manufacturer's run time estimate, and any other media specific issues. The FTO shall prepare an arsenic specific sampling plan that addresses collection of several samples near the breakthrough point and considers the frequency of arsenic speciation analysis.

The FTO must consider collecting samples for arsenic measurement on a regular basis (e.g. weekly) during the beginning and middle portions of the Adsorption Capacity Verification Test, and then more frequently as the media approaches capacity. One option is to use field test kits to monitor arsenic, which can provide immediate information on the arsenic concentrations in the treated water. These kits are not acceptable for final verification data, but can be used to indicate when arsenic is increasing in the treated water and the media is nearing capacity. This information can be used to indicate that increased sampling frequency should be initiated in anticipation of breakthrough. If the use of arsenic test kits is planned, it is important to select a kit that has a detection limit, accuracy, and precision that will provide meaningful data at the concentrations expected in the treated water. The FTO may also consider collecting samples for arsenic on a more frequent basis (daily or three times per week) as the media approaches capacity, but not analyzing all the samples. Arsenic samples can be preserved and held (for total arsenic, as well as soluble arsenic and speciated arsenic if field speciated and preserved) for later analysis. In this approach, only selected samples (e.g. one per week) would be analyzed. Once the results are received, additional samples could be scheduled for analysis to "fill in" the data, as the breakthrough curve begins to rise and capacity is approached. A "sample and hold" plan can be a cost effective approach for long run time tests. The FTO sampling and analysis plan for arsenic should incorporate a schedule that will provide a minimum of five samples to represent the 80 to 100 percent portion of the breakthrough curve. It is recommended that the sampling plan include increased sampling frequency as the media approaches 70 percent of the predicted capacity.

The arsenic sampling plan shall also include a schedule for collection of samples for arsenic speciation. As described in Section 7.3, the species of arsenic (III or V) present in the feed water can have a direct impact on the performance of adsorptive processes. The frequency of performing arsenic speciation will depend on the source water and the specific media. At a minimum, three samples of the feed water and treated water, collected at regular intervals over the duration of the Adsorption Capacity Verification Test, shall be speciated. More frequent arsenic speciation may be needed depending on the actual distribution of the arsenic species in the feed water, and the importance of the arsenic species (III or V) to the performance of a

specific treatment process. If the feed water has only one species of arsenic present, then the minimum frequency may be appropriate. However, if the source water has significant concentrations of both species present, and/or the media performance is dependent on the arsenic species, then more frequent arsenic speciation should be proposed by the FTO to properly monitor the system performance. If both species of arsenic (III and V) are present in the source water, then it is expected that at least 25 percent of the samples collected during the Adsorption Capacity Verification Test will be speciated.

Sample collection procedures for intermittent flow systems must ensure that freshly treated water is collected and not water that was stagnant in the bed. For intermittent flow systems, sample collection should occur during a continuous flow period after a minimum of 10 bed volumes has passed through the system or after one hour of continuous flow. If a system is not normally operated for at least 10 bed volumes or one hour (such as an intermittent system that is only “on” for a few minutes each hour), then the system shall be operated manually during sample collection to meet this requirement.

For media that requires regeneration, the FTO shall specify the sample collection frequency and sample type to characterize the regeneration process. At a minimum, sampling of the regenerative water for the parameters listed in Table 5 shall be done on a composite sample. The composite should be a flow weighted composite sample of the regeneration fluid. If grab samples are being taken to make a composite, a minimum of six samples should be collected over the regeneration period. It is important that the sample be representative of the entire regeneration fluid volume so that an accurate determination of the mass of arsenic recovered in the regeneration process can be determined. Other parameters may be important for monitoring the effectiveness of the regenerative liquid, or the performance of the regeneration step. These additional parameters should be added as appropriate to the specific media being verified.

Following the completion of media regeneration, the system shall be operated for at least four weeks. The sampling plan developed for all parameters and specifically for arsenic should include this post-regeneration operating period. The sampling plan should include the collection of sufficient samples to provide a basis for comparison to the original performance of the media, and determine if the media has been impacted by regeneration. The post-regeneration monitoring plan shall specify the collection of samples at the same frequency as for the Adsorption Capacity Verification Test (Table 5) or more frequently if needed to characterize the water after regeneration. In addition, total arsenic samples will be collected at a minimum of three times during the first week of the post regeneration period test. More frequent monitoring of selected parameters may be needed and proposed by the FTO. As an example, certain activated alumina media can release elevated levels of aluminum after regeneration. In this case, sampling for aluminum every four hours for the first day and daily for a week may be appropriate. An arsenic speciation test shall be performed at least once during the post regeneration test period. More frequent speciation shall be performed if more frequent arsenic speciation was part of the arsenic speciation plan, as described earlier in this section.

At the end of Task 2A, samples of the media shall be collected to assess the chemical content for disposal purposes. At least one representative sample of the media shall be collected and sent to the laboratory for the Toxicity Characteristic Leaching Procedure (TCLP) and the California

Waste Extraction Test (WET). The sample of the media shall be collected in a manner that ensures that a cross section of all the media (a composite sample over the entire depth of the column) is included in the sample sent to the laboratory. It may be necessary to place the media from the column in a container and mix it prior to sampling, or it may be necessary to “core” the column to collect a representative sample. The FTO shall describe the sampling procedures that will be used to ensure that a representative sample of the media is collected for these analyses.

8.4 Analytical Schedule

Operational Data Collection. The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include at a minimum flow rates, head loss (or pressure), chemicals used (including feed volume and dosage), and hours of operation per day. Operational data monitoring frequencies are described in Table 2. The FTO shall include acceptable values and ranges for all operational parameters monitored.

Operational parameters shall also be specified for the regeneration requirements for the system. Operational parameters shall include at a minimum, regenerate solution composition, flow rate and volume of regenerate, rinse solution composition, flow rate, and volume, measurement of media quantity before and after regeneration, and any operating parameters specified by the manufacturer for control of the regenerative process. The FTO shall include acceptable values and ranges for these operational parameters and monitoring requirements.

Water Quality Data Collection. During Adsorption Capacity Verification Testing, the adsorptive media feed water quality and treated water quality shall be characterized by analysis of the water quality parameters listed in Table 5. The sampling frequency described in Table 5 and as discussed in the previous section, is intended to provide sufficient water quality data to effectively characterize the breakthrough profile for arsenic. Additional or more frequent analyses may be stipulated at the discretion of the FTO.

As described earlier in Section 7.4, it is important when selecting the analytical methods for the various parameters that the procedures can achieve detection and reporting limits that are appropriate to meet the objectives of the test. As an example, some arsenic test methods can only detect arsenic above 0.010 mg/L. If the performance of the technology is being verified to meet drinking water standards of 0.010 mg/L, and the capacity test is based on a maximum treated water level of 0.010 or 0.012 mg/L, then a method with a detection limit of 0.010 mg/L would not be appropriate or useful. The selection of each test method must consider how the data will be used, the objectives of the PSTP, and the ability of the method to meet the accuracy and precision objectives specified in the PSTP.

The sample of media that is collected for TCLP and California WET shall have the following metals analyzed in the leachate from these procedures: As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, and Zn.

8.5 Evaluation Criteria and Minimum Reporting Requirements

At a minimum, breakthrough curves (adsorptive media effluent concentrations versus bed volumes) for arsenic concentrations should be presented. Include plotted adsorptive media influent parameter concentrations versus bed volumes on the same plot. Calculate and tabulate average influent parameter concentrations. A sample form for reporting data is illustrated in Table 6. For media requiring regeneration, the data from the post regeneration period will be compared to the first four weeks of operation with fresh media. The data will be evaluated for evidence of reduced performance after regeneration.

Tabular records for the adsorptive media influent and effluent arsenic, pH, pressure, and all other monitored parameters and constituents shall be maintained and presented. Results shall include adsorptive media influent and effluent average, minimum, and maximum; and for sample sets of eight or more the results shall also include the standard deviation and confidence interval for each analyte.

9.0 TASK 2B: REGENERATION VERIFICATION TESTING (OPTIONAL)

9.1 Introduction

This task is applicable only to adsorption treatment systems that use adsorptive media that can be regenerated in-place and that incorporate regeneration capability as an integral part of the equipment being tested. If the manufacturer wishes to evaluate the in-place regeneration capability of the equipment, verification testing must include, as a minimum, two complete cycles: an initial loading cycle, followed by a regeneration cycle (which is part of Task 2A), and then a second loading cycle, followed by a second regeneration cycle. This allows for a comparison of adsorptive media performance before and after regeneration. Furthermore, the regeneration efficiency shall be determined based on the second regeneration cycle.

Verification of in-place regeneration based on two or more complete loading/regeneration cycles is recommended, if possible. However, the length of time between regeneration cycles may preclude multiple cycles being tested.

Guidelines for modified testing to evaluate an in-place regeneration are described within this task. The regeneration step, regeneration fluids used, and regeneration procedure shall be documented as part of the Equipment Characteristics (Chapter 1, Section 4.2).

9.2 Experimental Objectives

The objectives of this task are to evaluate adsorptive media performance after regeneration, evaluate regeneration efficiency, evaluate operational details of media regeneration, and characterize any residuals produced during regeneration.

The FTO shall identify in the PSTP the treated water quality performance to be achieved after regeneration of the media, and any specific criteria concerning the regeneration process, such as

quantity of regenerate used, time to regenerate the media, etc.

9.3 Work Plan

To verify a manufacturer's stated performance capability regarding the in-place regeneration capability of adsorption equipment, verification testing shall be conducted as described in Task 2A, Section 8, combined with the additional requirements or modifications as described in this task. The testing period shall include, as a minimum, two complete cycles: an initial loading cycle, followed by a regeneration cycle, and then a second loading cycle, followed by a second regeneration cycle. During each loading period, the adsorptive media system must be operated at least until breakthrough of arsenic, based on the treatment capability defined in the manufacturer's statement of performance as described in Section 8.2.

The source water arsenic concentration shall be the same during both loading cycles. The testing conditions shall also be identical during both loading cycles. All other experimental parameters, such as water source, pretreatment, etc. shall be as similar as possible during the two (or more, if necessary) loading cycles. If the four-step cycle is completed in less than 60 days, additional loading/regeneration cycles shall be performed until the total run time is at least 60 days.

The work plan for this task shall follow the same approach as for Task 2A, Section 8.3 and will run in conjunction with Task 2A. The results from the first loading and regeneration cycle for this task will be the same as Task 2A. Under this task, the second loading cycle will begin after the first regeneration of the media and continue until the second loading and regeneration cycles are complete. All aspects of the work plan for Tasks 2A, Section 8.3, shall be incorporated into the work plan for this task.

If possible, incorporation of additional cycles into the testing program would increase the amount of data on regeneration effectiveness and retention of adsorption capacity over time. Whether or not additional cycles are completed, the FTO must make a statement about the long-term efficiency of regeneration for the adsorptive media tested. If the long-term efficiency of regeneration is not studied as part of this testing program, or not available from other studies, a statement by the FTO is required indicating that the long-term regeneration efficiency is unknown. For adsorptive media that has been well studied, a statement on the long-term regeneration efficiency can be based on the results of previous peer-reviewed published studies. See Section 4.2.2. for information on using available data.

Any residuals produced during in-place regeneration of the adsorptive media shall be fully characterized and documented with respect to quantity and composition. The information from this residuals characterization task shall be used to determine the efficiency of regeneration. For example, if a low pH solution is used to remove arsenic from the media, this solution shall be monitored for arsenic content and other ions of interest. If a rinsing solution is used, then this liquid will also be measured for arsenic concentration and other ions of interest. A mass balance approach shall be used to determine whether all the arsenic was removed during the regeneration process. The regeneration efficiency and the adsorbent usage rate for each cycle shall be reported.

Under Task 2A a sample of the media shall be taken for TCLP and California WET testing at the end of the verification period. If Task 2B is part of the verification process, the sample of the media for this testing will be deferred until the end of the regeneration verification process. The same sampling and analysis plan shall be followed as outlined in Task 2A, Section 8.3

Operational Data Collection. The FTO shall provide written procedures, the same as under Task 2A, Section 8.3, describing the operational parameters that should be monitored, monitoring locations, and the frequency of monitoring. Such operational parameters shall include at a minimum flow rates, and head loss (or pressure), chemicals used (including feed volume and dosage), and hours of operation per day. Operational data monitoring frequencies are described in Table 2. The FTO shall include acceptable values and ranges for all operational parameters monitored. The collection of operational data shall continue during the second and any subsequent loading cycles, following the same procedures as set forth for Task 2A, Adsorption Capacity Verification Test.

Operational parameters shall also be specified for the regeneration requirements for the system. Operational parameters shall include at a minimum, regenerate solution composition, flow rate and volume of regenerate, rinse solution composition, flow rate, and volume, measurement of media quantity before and after regeneration, and any operating parameters specified by the manufacturer for control of the regenerative process. The FTO shall include acceptable values and ranges for these operational parameters and monitoring requirements.

Water Quality Data Collection. During the Regeneration Verification Testing, the adsorptive media feed water quality and treated water quality shall be characterized during all loading cycles by analysis of the water quality parameters listed in Table 5 and in accordance with sampling schedule and approach given in Section 8.3. The sampling frequency described in Table 5 and in the Section 8.3 is intended to provide sufficient water quality data to effectively characterize the breakthrough profile for arsenic for each loading and regeneration cycle. Additional or more frequent analyses stipulated at the discretion of the FTO for Task 2A shall also apply to additional loading cycles under this task.

It is possible that the results obtained on media capacity and source water variability during the first loading cycle may indicate that a reduced or more focused sampling program could be used in subsequent loading cycles. The FTO can propose a reduced sampling frequency for some or all parameters based on the results from Task 2A. This request will be reviewed by NSF and, if appropriate, NSF may approve the change in sampling frequency. However, the FTO shall incorporate the same testing plan as planned for Task 2A, Section 8.3 in the PSTP. Only after the first loading and regenerative cycles are complete, and the results available, will a request for a change in the sampling plan be considered. If the sampling plan for Task 2A is modified during the first loading cycle, then the modification will also apply to this task and to subsequent loading cycles.

9.4 Analytical Schedule

Influent and effluent sampling and analysis requirements described in Section 8.4 for Task 2A and Table 5 shall be applied to *each* loading cycle to assess arsenic breakthrough and other water

quality parameters. For characterization of regeneration residuals, a sampling and analytical plan shall be developed by the FTO in the PSTP to thoroughly characterize the content of the residual stream(s). Selection of parameters, in addition to arsenic and pH, for monitoring the regenerative liquids and solids will be specific to the media and the regeneration process. The FTO shall include in the PSTP a discussion of the basis for the parameter selection for the regeneration residuals. The analytical program shall meet all of the Quality Assurance/Quality Control (QA/QC) requirements that apply to the previous Tasks (1 and 2A).

9.5 Evaluation Criteria and Minimum Reporting Requirements

Verification testing of adsorption treatment systems with in-place regeneration includes the same types of data analysis and interpretation as described previously in Section 8.5. In addition, a comparative analysis of adsorption characteristics before and after media regeneration shall be performed. The purpose of the comparative analysis is to assess and quantify whether any reduction in adsorptive media service life or adsorption capacity occurs because of in-place regeneration. This shall be evaluated by determining the media service life (operation time, throughput in bed volumes of water treated, and adsorbent usage rate until breakthrough), for the initial and subsequent loading periods and quantitatively comparing the results. Similarly, the adsorption capacity before and after regeneration can be determined and compared. In addition, a mass balance for arsenic should be developed to evaluate the regeneration efficiency. A general equation that describes the regeneration efficiency is:

$$E_R = \frac{q \cdot m_A}{m_R} \quad (1)$$

where: E_R is the regeneration efficiency,
 q is the adsorption capacity,
 m_A is the mass of adsorbent, and
 m_R is the mass arsenic recovered in the regeneration stream.

The regeneration efficiency shall be calculated after each regeneration cycle.

10.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

10.1 Introduction

During each day of verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. In addition, the performance of the water treatment equipment shall be documented, including rate of head loss gain. The volumetric flow rate through an adsorptive media vessel is a critical parameter, and must be monitored and documented. Adsorptive media performance is affected by the EBCT, which varies directly with the volumetric flow rate through the vessel.

10.2 Experimental Objective

The objective of this task is to accurately and fully document the operating conditions during treatment, and the performance of the equipment. This task is intended to result in data that describe the operation of the equipment and data that can be used to develop cost estimates for operation of the equipment.

This task shall be performed in conjunction with Task 1, System Integrity Verification Testing, and in conjunction with Task 2A, Adsorption Capacity Verification Testing. This task will also be performed in conjunction with Task 2B, Regeneration Verification Testing, if applicable.

10.3 Work Plan

During each day of verification testing [Task 1, System Integrity Verification Testing; Task 2A, Adsorption Capacity Verification Testing; and Task 2B, Regeneration Verification Testing (if applicable)], treatment equipment operating parameters for both pretreatment and adsorptive media shall be monitored and recorded on a routine basis. This shall include a complete description of pretreatment chemistry and all other applicable data.

Electrical energy consumed by the treatment equipment shall be measured, or as an alternative, the aggregate horsepower of all motors supplied with the equipment could be used to develop an estimate of the maximum power consumption during operation. Performance shall be evaluated to develop data on chemical dosages needed and on energy needed for operation of the process train being tested.

A complete description of the treatment process shall be given, with data on points of chemical addition, and volume and detention time of each process vessel at rated flow if applicable. Data on the adsorptive media vessel shall be provided and shall include the EBCT, depth, effective size, and uniformity coefficient of each layer of adsorptive media and support material. The type and source of adsorptive media used and the type of support material used shall be stated.

10.4 Schedule

Tables 2 and 3 present the schedule for observing and recording equipment operation and performance data. The schedule applies to System Integrity Verification Testing, Adsorption Capacity Verification Testing, and Regeneration Verification Testing.

10.5 Evaluation Criteria

Operating conditions and performance data will be tabulated for inclusion in the ETV verification report.

11.0 TASK 4: DATA MANAGEMENT

11.1 Introduction

The data management system used in the verification testing program shall involve the use of

computer spreadsheet software and manual recording of operational parameters for the adsorptive media and pretreatment equipment on a daily basis.

11.2 Experimental Objective

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the FTO provides sufficient and reliable operational data for verification purposes.

11.3 Work Plan

The following section has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of the computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters. In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of adsorptive media operation. At a minimum, backup of the computer databases to diskette should be performed on a weekly basis.

In the case when a SCADA system is not available, field testing operators shall record data and calculations by hand in laboratory notebooks. (Daily measurements shall be recorded on specially-prepared data log sheets as appropriate.) The laboratory notebook shall provide carbon copies of each page. The original notebooks shall be stored on-site; the carbon copy sheets shall be forwarded to the project engineer of the FTO at least once per week during testing period. This protocol will not only ease referencing the original data, but offer protection of the original record of results. Operating logs shall include a description of the treatment equipment (description of test runs, names of visitors, description of any problems or events, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

The database for the project shall be set up in the form of custom-designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time. Following data entry, the spreadsheet shall be printed out and the print out shall be checked against the handwritten data sheet. Any corrections shall be noted on the hard copies and corrected on the screen, and then a corrected version of the spreadsheet shall be printed out. Each step of the verification process shall be initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (i.e., System Integrity Verification Testing runs, Adsorption Capacity, and Regeneration Verification Testing runs) shall be assigned a run number which will then be permanently associated to the data from the experiment through each step of data entry and analysis. As samples are collected and sent to a laboratory that is certified, accredited or

approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA, the data shall be tracked by use of the same system of run numbers. Data from the outside laboratories shall be received and reviewed by the field testing operator. These data shall be entered into the data spreadsheets, corrected, and checked in the same manner as the field data.

12.0 TASK 5: QUALITY ASSURANCE/QUALITY CONTROL

12.1 Introduction

QA/QC of the operation of the water treatment system, adsorptive media vessels, instrumentation, and the measured water quality parameters shall be maintained during the verification test.

12.2 Experimental Objective

The objective of this task is to maintain strict QA/QC methods and procedures during the equipment verification testing program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to determine exact conditions at the time of testing.

12.3 Work Plan

When developing the Quality Assurance Project Plan (QAPP) within the PSTP, the FTO should refer to Chapter 1, Section 6.0 Quality Assurance Project Plan in addition to the information provided herein. All of the requirements and guidelines described in Chapter 1 shall be included in the development of the PSTP. In addition to the general ETV Program QA/QC described in Chapter 1, the PSTP shall incorporate the specific adsorptive media QA items detailed in this section.

Equipment flow rates and associated signals should be checked and recorded on a routine basis. A routine daily walk through during testing shall be established to confirm that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to confirm that any chemicals are being fed at the defined flow rate into a flowstream that is operating at the defined flow rate, such that the chemical concentrations are correct. In-line monitoring equipment such as flowmeters, etc. shall be calibrated to confirm that the readout matches with the actual measurement (i.e. flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods or specified by the FTO.

It is extremely important that system flow rates are maintained at set values and monitored frequently. Doing so allows a constant and known EBCT to be maintained in the adsorptive media vessel. Adsorptive media performance is directly affected by the EBCT, which in turn is proportional to the volumetric flow rate through the contactor. Therefore, an important QA/QC objective shall be the maintenance of a constant volumetric flow rate through the adsorptive media vessel by frequent monitoring and documentation. Documentation shall include an

average and standard deviation of recorded flow rates through the adsorptive media vessel.

12.3.1 Daily QA/QC Checks

- Chemical feed pump flow rates, if applicable;
- In-line pH, pressure and temperature (check calibration);
- System adsorptive media vessel flow rate (checked volumetrically over a specific period of time to confirm instrument reading at least two times daily, approximately four hours apart for applications where the treatment system is expected to operate continuously, or once daily where the treatment system is expected to operate intermittently);
- In-line turbidimeter flow rate checked daily by volumetric measurement over a specific period of time to confirm instrument reading; and
- In-line turbidimeter readings checked daily against a properly calibrated bench-top model.

12.3.2 Weekly QA/QC Checks

- In-line flow meters/rotameters (confirm flow rate volumetrically over a specific period of time to confirm instrument reading, and if necessary, clean equipment to remove any foulant buildup);
- In-line turbidimeters (clean out reservoirs, if necessary, and recalibrate);
- Differential pressure transmitters (check gauge readings and electrical signal using a dead weight calibration tester); and
- Tubing (check condition of all tubing and connections, replace if necessary).

12.3.3 QA/QC Checks Performed Each Testing Period

- Performance evaluation check of the resin columns used during arsenic speciation procedures (see Appendix A).

12.4 Analytical Methods

The analytical methods utilized in this study for on-site and off-site monitoring of adsorptive media influent and effluent water quality are described in the sections below and presented in Tables 1 and 5. If new methods are published and approved or current methods updated, the most current methods shall be used. Use of either bench-top or in-line field analytical equipment will be acceptable for on-site analyses for the verification testing; however, in-line equipment is recommended for ease of operation. Use of in-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques.

Temperature, pH, alkalinity, and turbidity must be analyzed on-site immediately after sample collection. Other parameters, such as calcium, magnesium, hardness and fluoride can be performed either on-site or in the laboratory, as long as the holding time requirements are met.

All other analyses shall be performed in a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA. All samples collected for laboratory analysis, including arsenic chloride, sulfate, silica, aluminum, sodium, iron, manganese and additional parameters, shall be collected and preserved in accordance with *Standard Method* 3010 B, paying particular attention to the sources of contamination as outlined in *Standard Method* 3010 C. The samples should be refrigerated at approximately 2 to 8°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 2 to 8°C. Samples shall be processed for analysis within EPA approved holding times, which must be included in the PSTP. The laboratory shall keep the samples at approximately 2 to 8°C until initiation of analysis.

Arsenic speciation using the Battelle method (Appendix A) is an important part of the verification test. In addition to all normal QA requirements for handling field samples and for arsenic determination, a special check of the resin used for the speciation procedure is required. The resin must be prepared properly in accordance with the procedures given in the method, and the capability of the resin to properly separate arsenic III from V must be demonstrated. It cannot be assumed that a batch of resin has been properly prepared without validating the separation process using water spiked with known concentrations of arsenic III and V. This QC check should include having the laboratory make a solution with a mixture of arsenic III and V, having the field staff perform the separation using their standard procedures, and then having the laboratory analyze the samples for arsenic III and V. The results of the QC check sample must demonstrate the separation procedure is working properly. This check must be done for each new batch of resin used during the verification test.

The FTO shall prepare tables summarizing the pertinent QA information and the objectives/acceptance limits for accuracy and precision. These tables shall show at minimum, the methods to be used, the method detection limits, the number of field and lab duplicates, the number of laboratory spikes/blanks, the acceptable precision as a percent, the acceptable accuracy as a percent recovery range, and calibration information that impacts accuracy, such as frequency and method for calibrating the pH meter, the turbidimeter, etc.

12.4.1 Arsenic

Laboratory analyses for arsenic shall be performed in accordance with EPA Method 200.8. These analyses are the most critical for the entire ETV procedure. When arsenic species are to be analyzed, the samples shall be collected and preserved in accordance with the Protocol for Arsenic Speciation developed by Battelle for the EPA, as found in Appendix A of this protocol. EPA Method 200.8 has been specified because of the need to achieve low detection limits (0.002 to 0.004 mg/L) with good accuracy and precision for this verification test. Other EPA approved drinking water methods that can achieve these low laboratory reporting limits with comparable accuracy and precision may be proposed by the FTO. Minimum analytical turn around time is required to achieve optimum process control. Please note when using this method that ultra-pure (optimum) grade sulfuric acid must be used (not reagent grade) to avoid the trace amounts of arsenic that can be present in reagent grade sulfuric acid.

12.4.2 pH

Analyses for pH shall be performed on-site according to *Standard Method* 4500-H⁺ B (Electrometric Method) or EPA Methods 150.1 and 150.2. A three-point calibration of the pH meter used in this study shall be performed once per day when the instruments are in use. Certified pH buffers in the expected range shall be used. The pH probes shall be stored in the appropriate solution defined in the instrument manual. If pH is adjusted in the process, pH readings are required before and after each pH adjustment.

12.4.3 Alkalinity

Analyses for alkalinity shall be performed on-site according to *Standard Method* 2320 B (Titration Method).

12.4.4 Fluoride

Analyses for fluoride shall be performed on-site or in the lab according to *Standard Method* 4110 B, 4500-F⁻ B, 4500-F⁻ C (Ion-Selective Electrode Method), 4500-F⁻ D, or EPA Method 300.0.

12.4.5 Chloride

Analyses for chloride shall be performed in the lab according to *Standard Method* 4110 B, 4500-Cl⁻ B (Argentometric Method) or 4500-Cl⁻ D (Mercuric Nitrate Method) or EPA Method 300.0.

12.4.6 Sulfate

Analyses for sulfate shall be performed in the lab according to *Standard Methods* 4110 B, 4500 SO₄²⁻ C, 4500 SO₄²⁻ D, 4500 SO₄²⁻ E (Turbidimetric Method), or 4500 SO₄²⁻ F, or EPA Methods 300.0 or 375.2.

12.4.7 Silica

Analyses for silica shall be performed in the lab according to *Standard Method* 3120 B, 4500-Si C, 4500-Si D (Molybdosilicate Method), or 4500-Si E, or EPA Method 200.7.

12.4.8 Aluminum

Analyses for aluminum shall be performed in the lab according to *Standard Method* 3120 B or EPA Methods 200.7, 200.8, or 200.9.

12.4.9 Sodium (Optional)

Analyses for sodium shall be performed in the lab according to EPA Method 200.7.

12.4.10 Calcium

Analyses for calcium shall be performed on-site or in the lab according to *Standard Methods* 3120 B or 3500-Ca B (EDTA Titrimetric Method), or EPA Method 200.7.

12.4.11 Hardness

Analyses for hardness shall be performed on-site or in the lab according to *Standard Method* 2340 C (EDTA Titrimetric Method).

12.4.12 Magnesium

Analyses for magnesium shall be performed on-site or in the lab according to *Standard Method* 3120 B or 3500-Mg B (Calculation Method), or EPA Method 200.7.

12.4.13 Iron

Analyses for iron shall be performed in the lab using *Standard Method* 3120 B or EPA Methods 200.7, 200.9.

12.4.14 Manganese

Analyses for manganese shall be performed in the lab using *Standard Method* 3120 B or EPA Methods 200.7, 200.8, 200.9.

12.4.15 Turbidity

Turbidity analyses shall be performed on-site according to *Standard Method* 2130 B or EPA Method 180.1 with either an in-line or a bench top turbidimeter. In-line turbidimeters shall be used for measurement of turbidity in the treated waters, and either an in-line or bench-top turbidimeter may be used for measurement of the feedwater.

During each verification testing period, the in-line and bench-top turbidimeters shall be left on continuously. Once each turbidity measurement is complete, the unit shall be switched back to its lowest setting. All glassware used for turbidity measurements shall be cleaned and handled using lint-free tissues to prevent scratching. Sample vials shall be stored inverted to prevent deposits from forming on the bottom surface of the cell. The FTO shall document any problems experienced with the monitoring turbidity instruments, and shall also document any subsequent modifications or enhancements made to monitoring instruments.

12.4.15.1 Bench-top Turbidimeters. Grab samples shall be analyzed using a bench-top turbidimeter. Readings from this instrument shall serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of verification testing and on a weekly basis using primary turbidity standards of 0.1, 0.5, and 3.0 NTU. Secondary turbidity

standards shall be obtained and checked against the primary standards. Secondary standards shall be used on a daily basis to check calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

The method for collecting grab samples shall consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity. For the case of cold water samples that cause the vial to fog preventing accurate readings, the vial shall be allowed to warm up by partial submersion in a warm water bath for approximately 30 seconds.

12.4.15.2 In-line Turbidimeters. In-line turbidimeters shall be used for measurement of turbidity in the filtrate water during verification testing and must be calibrated and maintained as specified in the manufacturer's operation and maintenance manual. It will be necessary to check the in-line readings using a bench-top turbidimeter at least daily; although the mechanism of analysis is not identical between the two instruments, the readings should be comparable. Should the comparison suggest inaccurate readings, then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted, using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic check of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. The LED readout shall be checked that it matches the data recorded on the data acquisition system, if the latter is employed.

12.4.16 Temperature

Temperature shall be analyzed on-site according to *Standard Method 2550*.

12.4.17 TCLP

TCLP shall be performed in the laboratory on the spent media using SW-846 and EPA Method 1311, including method SW-846 6010B for As, Ba, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn; and method SW-846 7470A for Hg.

12.4.18 California WET

The California WET shall be performed in the laboratory on the spent media, including method SW-846 6010B for As, Ba, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn; and method SW-846 7470A for Hg.

12.5 Tests and Data Specific to Adsorptive Media Type Evaluated

The adsorptive media type used for testing shall be described by providing data on the adsorptive media type characteristics and tests listed in Table 4.

13.0 OPERATIONS AND MAINTENANCE

The following are recommendations for criteria for the evaluation of operations and maintenance (O&M) manuals for equipment employing adsorptive media for arsenic removal.

13.1 Operation

The manufacturer shall provide readily understood information on the required or recommended procedures related to the proper operation of the equipment including, but not limited to, the following:

Monitoring of Preconditioning of Adsorptive Media:

- Utilize manufacturer's procedure, which may vary depending upon adsorptive media selected;
- Backwash Parameters (flow rate, time, backwash water turbidity, etc.);
- Pretreatment chemical application (chemical concentration, time, and flow rate);
- Volume of wastewater; and
- Wastewater disposal requirements (see Regeneration Wastewater Disposal below).

Monitoring Operation:

- Feed water arsenic concentration;
- Feed water pH;
- Feed water adjusted pH;
- Feed water flow rate;
- Feed water pressure;
- Treated water arsenic concentration;
- Treated water pH;
- Treated water adjusted pH;
- Treated water pressure;
- Chemical feed rates;
- Chemical consumption;
- Electrical energy consumption;
- Maintenance and operator labor requirements; and
- Spare parts requirements.

Monitoring Regeneration of Adsorptive Media:

- Utilize manufacturer's procedure for regeneration, which shall vary depending upon selected adsorptive media, equipment, and process variables;
- Backwash parameters (flow rate, time, backwash water turbidity, etc.);
- Regeneration parameters (flow rate, time, regeneration chemical concentration and flow rate, effluent arsenic concentration, effluent pH, etc.);
- Neutralization (or transition to Arsenic Removal Treatment Mode) Parameters (flow rate,

- time, neutralization chemical concentration and flow rate, effluent arsenic concentration, effluent pH, adsorptive media depletion, etc.); and
- Adsorptive media makeup requirement.

Monitoring Regeneration Wastewater Disposal:

- Utilize manufacturer's procedure for processing, reclaiming, and/or disposing of regeneration wastewater, adsorptive media preconditioning wastewater, and waste solids, which shall vary depending upon selected adsorptive media, equipment, treatment chemicals and process variables;
- pH adjustment parameters (flow rate, pH, time, pH adjustment chemical consumption, etc.);
- Flocculation/coagulation parameters (flow rate, time, flocculation/coagulation chemical consumption, etc.);
- Liquid/solid separation parameters (flow rate, time, etc.);
- Solids dewatering parameters (flow rate, time, sludge conditioning chemical consumption, dewatered sludge solids, content, toxicity of dewatered solids, etc.);
- Solids disposal parameters (volume, toxicity, permits, transportation of solids to disposal site, costs of transportation and disposal, etc.); and
- Liquid disposal parameters (volume, toxicity, pH, permits, adjustment requirements, costs of disposal, etc.).

13.2 Maintenance

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for each piece of operating equipment including, but not limited to:

- Pumps;
- Valves;
- All chemical feed and storage equipment; and
- All instruments.

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for non-mechanical or non-electrical equipment including, but not limited to:

- Adsorptive media vessels;
- Feed lines; and
- Manual valves.

14.0 REFERENCES

"California Code of Regulations." California Office of Administrative Law. 2003. <http://ccr.oal.ca.gov>.

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Standard Methods for the Examination of Water and Wastewater. 1999. 20th edition. APHA, AWWA, and WEF, Washington, D.C.

USEPA. 1996a. ICR Manual for Bench- and Pilot-Scale Treatment Studies. Technical Support Division, Office of Ground Water and Drinking Water, Environmental Protection Agency.

Table 1. Required Water Quality Analyses and Minimum Sample Frequencies for Task 1 System Integrity Verification Testing

Parameter	Frequency	Location	Standard Method ^a	EPA Method ^b
Adsorptive Media Influent and Effluent				
Arsenic	Daily	Lab		200.8
Arsenic Speciation	Three times during this task, twice during Startup and Shakedown	On-Site Prep ^c , Lab analyses	Not applicable	Battelle Speciation Method ^c , 200.8
Arsenic Test Kit	Optional by FTO	On-Site	Not applicable	Not applicable
pH	Daily	On-Site	4500-H ⁺ B	150.1, 150.2
Alkalinity	Daily	On-Site	2320 B	
Fluoride	Daily	On-Site, Lab ^d	4110 B, 4500-F ⁻ B, C, & D	300.0
Chloride	Weekly	Lab	4110 B, 4500-Cl ⁻ B & D	300.0
Sulfate	Weekly	Lab	4110 B, 4500-SO ₄ ²⁻ C, D, E, & F	300.0, 375.2
Silica	Daily	Lab	3120 B, 4500-Si C, D, & E	200.7
Aluminum	Daily	Lab	3120 B	200.7, 200.8, 200.9
Sodium (Optional)	Weekly	Lab		200.7
Calcium	Weekly	On-Site, Lab ^d	3120 B, 3500-Ca B	200.7
Hardness	Weekly	On-Site, Lab ^d	2340 C	
Magnesium	Weekly	On-Site, Lab ^d	3120 B, 3500-Mg B	200.7
Iron	Weekly	Lab	3120 B	200.7, 200.9
Manganese	Weekly	Lab	3120B	200.7, 200.8, 200.9
Turbidity	Daily	On-Site	2130 B	180.1
Temperature	Daily	On-Site	2550	

^a Standard Methods Source: 20th Edition of *Standard Methods for the Examination of Water and Wastewater*, 1999, American Water Works Association (AWWA).

^b EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

^c Speciation Method developed by Battelle for EPA (see Appendix A).

^d On-Site or at Laboratory, must meet short holding time requirements.

Table 2. Schedule for Observing and Recording Equipment Operating and Performance Data

Operational parameter	Action
Feed water and adsorptive media vessel volumetric flow rate	When staffed, check and record every four hours, adjust when >5% above or below target. Record before and after adjustment.
Adsorptive media vessel head loss	Record initial clean bed total head loss at start of run and record total head loss every four hours, when staffed.
Electric power	Record meter daily.
Chemicals used	Record name of chemical, supplier, commercial strength, and dilution used for stock solution to be fed (if diluted) for all chemicals fed during treatment.
Chemical feed volume and dosage	Check and record once per day or more frequently if solution(s) made more frequently. Refill as needed and note volumes and times of refill.
Hours operated per day	Record in logbook at end of day or at beginning of first shift on the following workday. Any stoppage of flow to the adsorptive media vessel shall be recorded. Flow stoppage shall be accounted for by not including it in the cumulative operation time.

Test ID	Chemical Name	Initial Conc. (M)	Final Conc. (M)	Consumption (M)	Reaction Time (h)	Yield (%)	Purity (%)	Notes
SI-001	Hydrochloric Acid	1.0	0.5	0.5	2.0	85	92	Standard procedure
SI-002	Sulfuric Acid	0.8	0.3	0.5	1.5	78	88	Optimized conditions
SI-003	Nitric Acid	0.5	0.2	0.3	1.0	65	75	Controlled reaction
SI-004	Phosphoric Acid	0.3	0.1	0.2	0.8	55	65	Low temperature
SI-005	Acetic Acid	0.2	0.05	0.15	0.5	45	55	High purity required
SI-006	Formic Acid	0.1	0.02	0.08	0.3	35	45	Special handling
SI-007	Benzoic Acid	0.05	0.01	0.04	0.1	25	35	Highly reactive
SI-008	Salicylic Acid	0.02	0.005	0.015	0.05	15	25	Delicate compound
SI-009	Ascorbic Acid	0.01	0.002	0.008	0.02	10	20	Unstable in air
SI-010	Glucuronic Acid	0.005	0.001	0.004	0.01	5	10	Biological sample

MANUFACTURER _____ PRODUCT NAME _____ MODEL NO. _____

ADSORPTIVE MEDIA

MANUFACTURER'S CHEMICAL CONSUMPTION OBJECTIVE:

	Chemical "A"	_____	Gallons/1000gal
		-----	_____ Gallons/1000gal
	Chemical "X"	_____	Gallons/1000gal

[illegible]

^a Data assembled on this report provides information which yields chemical consumption per thousand gallons of treated water. This in turn is to be converted to cost of each chemical per thousand gallons of treated water.

^b Flow Totalizing Meter Reading (n) - Meter Reading (n-1) in minutes.

^c “X” represents the total number of chemicals utilized, therefore, if two chemicals are used, “X” becomes “B”, etc.

Table 4. Tests and Data Specific to Adsorptive Media Type Evaluated

Data	Parameter
Raw material used to make adsorptive media	
Method of manufacture:	Chemical processes Thermal processes Sizing / Screening methods Packaging methods
Preconditioning Procedure:	Wetting requirements Defining requirements Waste
Regeneration Procedure:	Backwash Chemical process Return to treatment mode Waste
Regeneration Results:	Adsorption capacity restored Adsorption media attrition Waste
Physical and chemical characteristics:	Percent voids Pore size Abrasion number Moisture (weight %) Particle size Sieve size, US sieve series Effective size Uniformity coefficient

Table 5. Required Water Quality Analyses and Minimum Sample Frequencies for Task 2A Adsorption Capacity Verification Testing

Parameter	Frequency	Location	Standard Method ^a	EPA Method ^b
Adsorptive Media Influent and Effluent^c				
Arsenic	Weekly & more frequent near breakthrough	Lab		200.8
Arsenic Speciation	Minimum of three times during this task	On-Site Prep ^d , Lab analyses	Not applicable	Battelle Speciation Method ^d , 200.8
Arsenic Test Kit	Optional by FTO	On-Site	Not applicable	Not applicable
pH	Daily	On-Site	4500-H ⁺ B	150.1, 150.2
Alkalinity	Daily	On-Site	2320 B	
Fluoride	Daily ^f	On-Site, Lab ^e	4110 B, 4500-F ⁻ B, C, & D	300.0
Chloride	Weekly	Lab	4110 B, 4500-Cl ⁻ B- & D	300.0
Sulfate	Weekly	Lab	4110 B, 4500-SO ₄ ²⁻ C, D, E, & F	300.0, 375.2
Silica	Daily ^f	Lab	3120 B, 4500-Si C, D, & E	200.7
Aluminum	Daily ^f	Lab	3120 B	200.7, 200.8, 200.9
Sodium (Optional)	Weekly	Lab		200.7
Calcium	Weekly	On-Site, Lab ^e	3120 B, 3500-Ca B	200.7
Hardness	Weekly	On-Site, Lab ^e	2340 C	
Magnesium	Weekly	On-Site, Lab ^e	3120 B, 3500-Mg B	200.7
Iron	Weekly	Lab	3120 B	200.7, 200.9
Manganese	Weekly	Lab	3120B	200.7, 200.8, 200.9
Turbidity	Daily	On-Site	2130 B	180.1
Temperature	Daily	On-Site	2550	
TCLP	Once	Lab		1311
CA WET	Once	Lab		Metals analysis by SW-846 6010B and 7470A ^g Special CA method Metals analysis by SW-846 6010B and 7470A ^g

^a Standard Methods Source: 20th Edition of *Standard Methods for the Examination of Water and Wastewater*, 1999, AWWA.

^b EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

^c Influent sampling shall occur at approximately the same time as effluent sampling for each parameter during equipment operation.

^d Speciation Method developed by Battelle for EPA (see Appendix A).

^e On-site or laboratory analysis acceptable, as long as short holding time requirement is met.

^f Sampling and analysis frequency may be reduced if data from Task 1 show influent and effluent are stable.

^g Metals analyses will include As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, and Zn.

Table 6. Adsorption Capacity Verification Data Report

MANUFACTURER _____ PRODUCT NAME _____ MODEL NO _____
 ADSORPTIVE MEDIA _____ RATED CAPACITY _____ mg/L/FT³

Date/Time	Minutes ^{a)}	Flow Rate (gpm)	Meter (gallons)	Meter ^{b)} (gallons)	Pressure ^{c)} (psig)	Feed Arsenic (mg/L)	Treated Arsenic (mg/L)	Arsenic Removed ^{d)} (mg)	Cumulative Arsenic Removed (mg)
<u>Start</u>									
1)									
2)									
3)									
4)									
n-3)									
n-2)									
n-1)									
<u>End</u>									
n)									

^a Time (n) - Time (n-1) in minutes.

^b Flow Totalizing Meter Reading (n) - Meter Reading (n-1) in gallons.

^c Influent pressure - effluent pressure (gauge reading differential pressure).

^d
$$\frac{[\text{Feed Arsenic (n)} - \text{Treated Arsenic (n)}] + [\text{Feed Arsenic (n-1)} - \text{Treated Arsenic (n-1)}]}{(2)} \times [\text{meter (n)}] \text{ in mg}$$

Appendix A

Protocol for Arsenic Speciation

PROTOCOL FOR ARSENIC SPECIATION

The following text presents the protocol to be used for arsenic speciation sampling and analysis during this project.

1.0 Scope and Application

Arsenic occurs in natural water in both the organic and inorganic forms. However, inorganic arsenic is predominant in natural water and is the most likely form of arsenic to exist at concentrations that cause regulatory concerns (Edwards et al., 1997). Inorganic arsenic is normally found in water supplies as an anion with acid characteristics in the trivalent [arsenite or As (III)] and pentavalent [arsenate or As (V)] forms. The valence is significant because most arsenic treatment technologies are more effective for the removal of arsenate than for arsenite.

Although total arsenic concentrations can be effectively preserved in field samples, the present status of preserving inorganic arsenic species in field samples is inconclusive. Preservation of total arsenic is accomplished by acidifying the sample to $\text{pH} < 2$ in the field. However, a high level of ambiguity exists when acids such as nitric acid (HNO_3) or hydrochloric acid (HCl) are used to preserve inorganic species of arsenic. Interconversion of As (III) and As (V) in samples preserved with 0.05 *N* HCl has been reported to occur within one day (Andreae, 1977). Another laboratory study conducted by Eaton et al. (1997) examined preservation of arsenic using ascorbic acid and HCl . This study concluded that there were no effective methods for preservation of As (III) and As (V) in water samples. Some researchers have used freezing of samples as a means of preserving the inorganic species of arsenic. However, freezing is not a cost-effective or practical method for field sampling.

Since the present status of preserving arsenic species indicates that there are no completely effective preservation methods, field speciation is required. Research by Clifford et al. (1983), Ficklin (1983), and Edwards et al. (1997) indicate that the use of an anion exchange resin column is an accurate and cost-effective field method for arsenic speciation. As (III) and As (V) recovery was shown to be consistently above 95% using an anion exchange column (Edwards et al., 1997). Therefore, the decision was made to utilize a field speciation technique similar to that used by Edwards et al. (1997).

The field speciation technique described in the following sections uses 0.45- μm pore size filters to remove "particulate" arsenic. Research done by Edwards et al. (1997) also using 0.45- μm pore size filters indicates that particulate arsenic may not be completely removed by this pore size filter. Therefore, the particulate arsenic found using a 0.45- μm pore size filter should be considered the lower bound for arsenic particulate.

The only laboratory analysis required using the field speciation technique is total arsenic. Inductively coupled plasma-mass spectrometry (ICP-MS) was chosen as the method for total arsenic analysis due to its low method detection limit (MDL), proven effectiveness, and relatively low cost.

2.0 Method Summary

The field speciation method described in the subsequent sections utilizes an anion exchange resin column to separate the soluble arsenic species, As (V) and As (III). The soluble portion of the sample is obtained by passing the sample through a 0.45- μm pore size filter. After filtration, the sample is acidified using 0.5 mL of ultra-pure sulfuric acid per L of sample (0.05% [volume/volume]) to lower the sample pH value to about 2. At this pH range, As (III) will be completely protonated as H_3AsO_3 (see Figure A-1) and As (V) will be present in both the ionic form (i.e., H_2AsO_4^-) and protonated form (i.e., H_3AsO_4) (see Figure A-2). As the acidified sample is run through the column, the resin retains the As (V) (Note that the resin will retain only H_2AsO_4^- and that H_3AsO_4 , when passing through the column, will be ionized to H_2AsO_4^- due to elevated pH values in the column caused by the buffer capacity of acetate exchanged from the resin) and the As (III) (i.e., H_3AsO_3) passes through the column. The acidified sample and the resin-treated sample are analyzed separately for total arsenic using ICP-MS. As (III) concentration is reflected by the total arsenic concentration of the resin-treated sample. As (V) concentration is the difference of the total arsenic concentration of the acidified sample and the total arsenic concentration of the resin-treated sample.

H_2SO_4 is used to acidify the sample because HCl may create undesirable chloride interference when using the ICP-MS and because there is concern that nitric acid may damage the resin or form nitric acid-arsenic redox couples (Edwards et al., 1997).

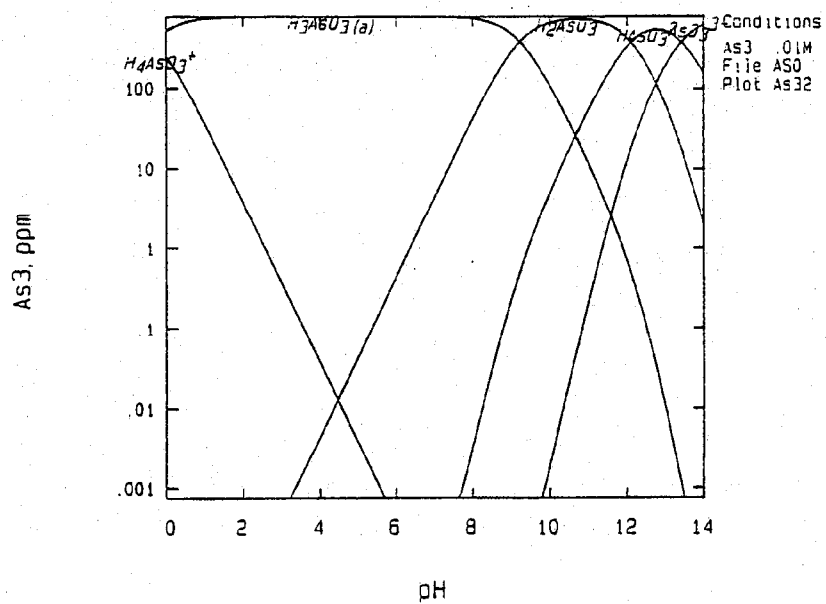


Figure A-1. Solubility Diagram of As (III)

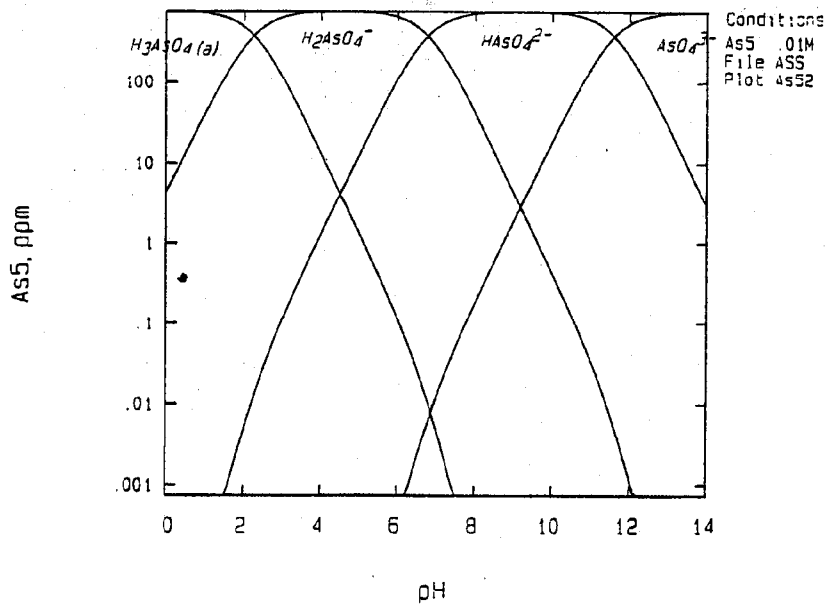


Figure A-2. Solubility Diagram of As (V)

3.0 Reagents

Reagents required for field speciation of arsenic include Dowex 1-X8, 50-100 mesh resin, acetic acid, sodium hydroxide (NaOH), and ultra-pure sulfuric acid and nitric acid. All chemicals are of reagent grade or higher.

3.1 Resin. Dowex 1-X8, 50-100 mesh resin will be used in this study.

3.2 Sodium Hydroxide. One (1) *N* NaOH will be used to prepare the resin.

3.3 Acetic Acid. One (1) *N* acetic acid will be used to prepare the resin.

3.4 Sulfuric Acid. An ultra-pure sulfuric acid (93-98%, sub-boiling distilled in quartz) will be used to acidify samples prior to the resin treatment.

3.5 Nitric Acid. An ultra-pure nitric acid (65%, sub-boiling distilled in quartz) will be used to preserve samples (see Table A-1)

4.0 Equipment/Apparatus

4.1 Resin Preparation. Dowex 1-X8, 50-100 mesh resin will be converted from the chloride form (as supplied by the manufacturer) to the acetate form before packing into columns. The resin will be prepared in batch according to the method used by Edwards et al. (1997). In summary, one kg of the resin will be placed in a 3-L beaker. One liter of 1 *N* NaOH will be added to the resin, stirred for an hour using an overhead stirrer, and drained. This NaOH rinse will be repeated three times in sequence. The NaOH-treated resin will then be rinsed twice with 1 L of deionized (DI) water, followed by an acetic acid rinse. The acetic acid rinse consists of adding 1 L of 1 *N* acetic acid to the resin, stirring for 5 minutes, and draining. The acetic acid rinse will be repeated three times in sequence. Finally, the mixture will be rinsed with 1 L of DI water three times in sequence.

4.2 Anion Exchange Column Preparation. Anion exchange columns will be prepared as described by Edwards et al. (1997). The columns selected for this field speciation method are 12 cm x 15 mm in size and made of polypropylene (Bio-Rad Laboratories, CA). Each column will

be slurry packed with approximately 20 grams (drained weight) of the prepared resin, yielding a resin depth of approximately 10.5 cm. The column will be capped with a plastic cap to prevent contamination prior to use.

4.3 Beaker. Four hundred-mL (400-mL) disposable plastic beakers will be used to collect raw water samples. All disposable beakers will be rinsed with DI water and air-dried before being packed into the sampling kits.

4.4 Syringe and Filter. Sixty-mL (60-mL) disposable plastic syringes with 0.45- μ m screw-on filters will be used to filter samples. All disposable syringes and filters will be rinsed with DI water and air-dried before being packed into the sampling kits.

4.5 Sample Bottles. VWRbrand™ TraceClean™ HDPE sample bottles (125 mL) labeled A, B and C will be used to contain unfiltered and acidified samples; filtered and acidified samples; and filtered, acidified, and resin-treated samples, respectively. Bottles A and C will contain appropriate amounts of concentrated ultra-pure nitric acid; whereas bottle B will contain 1.25 mL of 5% (volume/volume) ultra-pure sulfuric acid.

5.0 Sample Preservation, Containers, Handling, and Storage

Sample preservation, containers, handling, and storage requirements are indicated in Table A-1. Arsenic speciation at each sampling point in the water treatment process (e.g., inlet, pre-filtration, and outlet) will require collection of three 125-mL bottles identified as bottles A, B, and C, which are defined as follows:

- Bottle A will contain 125 mL of an unfiltered and acidified sample
- Bottle B will contain 125 mL of a filtered sample acidified with 1.25 mL of 5% H₂SO₄
- Bottle C will contain 20 mL of a sample obtained by passing some bottle B sample through an anion exchange resin column

Table A-1. Sample Preservation, Containers, Handling, and Storage

Sample Bottle Identifier	Sample Size	Container Type	Preservation	Analyte	Holding Time
A	125 mL	Certified HDPE	4°C HNO ₃ for pH<2	Total Arsenic by ICP-MS	6 months
B	125 mL	Certified HDPE	4°C 1.25 mL of 5% H ₂ SO ₄	Total Arsenic by ICP-MS	6 months
C	20 mL	Certified HDPE	4°C HNO ₃ for pH<2	Total Arsenic by ICP-MS	6 months

6.0 Procedure

The procedure for processing each arsenic speciation sample includes the following steps:

6.1 Raw Water Sample Collection. Completely fill bottle A with the water to be sampled. Cap bottle A and seal the lid with tape.

6.2 Filtered Sample Collection. Fill a 400-mL disposable plastic beaker with the water sampled in Section 6.1. Completely fill the syringe with the water from the plastic beaker. Screw the filter snug onto the end of the syringe and push the sample through the filter. Discard the first 10 drops to rinse the filter. Collect the filtered sample in bottle B. Remove the filter, refill the syringe with raw water, reattach the filter to the syringe, and push the sample through the filter into the bottle B. Repeat this process until bottle B is almost full; however, leave a small air gap at the top. The air gap should be approximately 1 to 5 mL. Cap bottle B tightly and shake the bottle for about 15 seconds to ensure thorough mixing. The air gap in the bottle allows the contents to mix thoroughly.

6.3 Resin-Treated Sample Collection. Remove the protective cap from the top of the resin column and break off the end at bottom of the resin column. Carefully fill the resin column to the top with the water in bottle B and let the column drain completely. Repeat this process until approximately 40 mL of water from bottle B has been passed through the column. Thereafter, position the resin column over bottle C, fill the column to the top, and let the entire column drain

into bottle C. Repeat this process until approximately 20 mL of resin-treated sample has been collected in bottle C. Cap bottles B and C and seal the lids with tape.

6.4 Sample Shipping. After the field speciation is complete, fill out a chain-of-custody form. Place all the sample bottles in a shipper with cold packs and have it shipped to Battelle via FedEx overnight delivery.

6.5 Arsenic Analysis. After the samples are received, Battelle will process the samples and perform arsenic analysis using ICP-MS according to EPA 200.8 method. The sample in bottle A will be digested prior to ICP-MS analysis, whereas the samples in bottles B and C will not be digested.

6.6 Graphic Speciation Procedure. Figure A-3 provides a graphic description of the field speciation procedure which is designed to assist plant POCs to follow the procedure more easily.

7.0 Calculations

For each As speciation sampling event, three sample bottles (A, B, and C) will be produced and the water in these bottles will be analyzed for total arsenic by ICP-MS. Total arsenic (including particulate arsenic), total particulate arsenic, total soluble arsenic, As (III), and As (V) will be calculated as follows:

- **Total Arsenic (including particulate arsenic)** = total arsenic concentration in bottle A
- **Total Soluble Arsenic** = total arsenic concentration in bottle B
- **Total Particulate Arsenic** = total arsenic concentration in bottle A – total arsenic concentration in bottle B
- **As (III)** = total arsenic concentration in bottle C
- **As (V)** = total arsenic concentration in bottle B – total arsenic concentration in bottle C

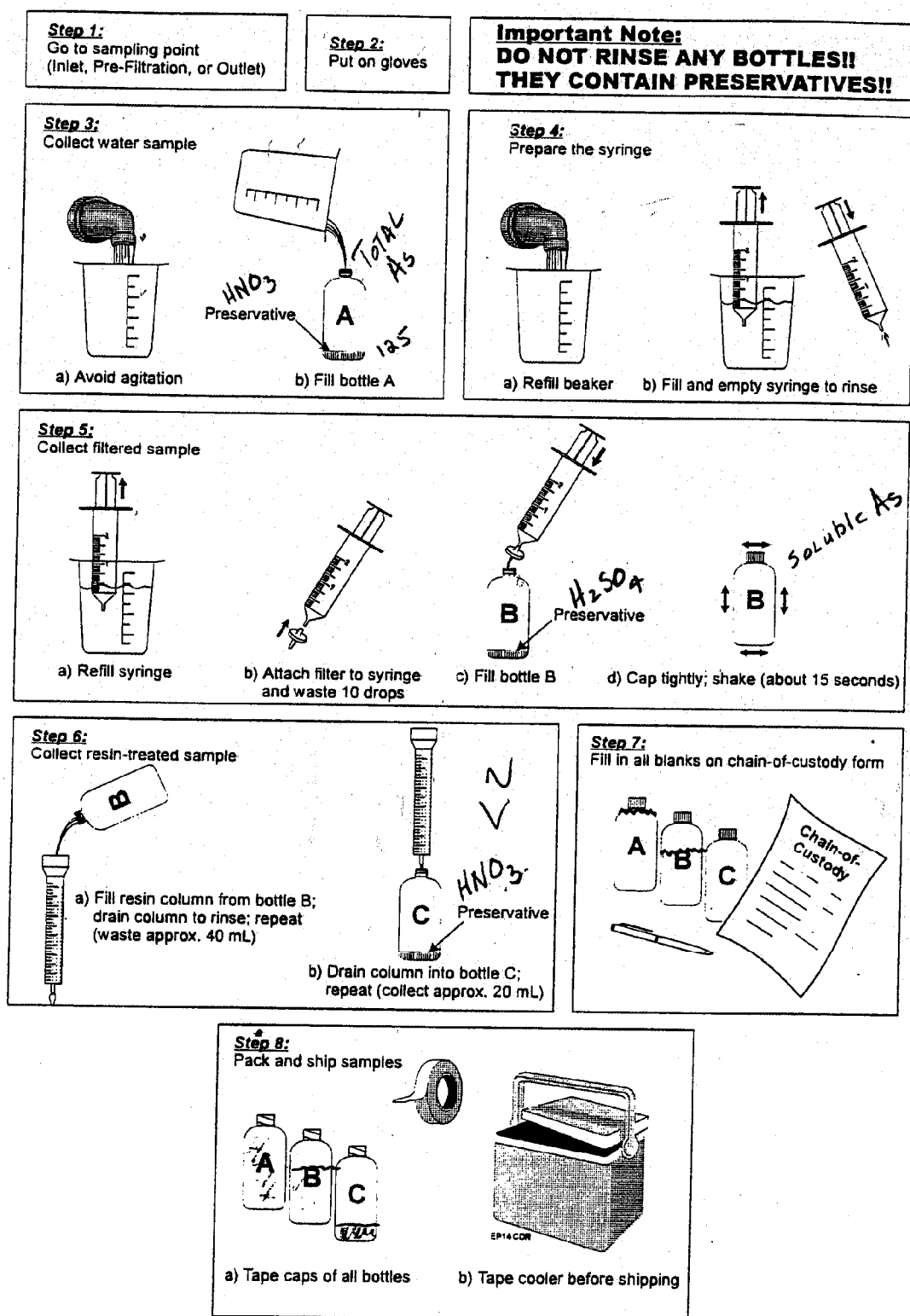


Figure A-3. Arsenic Field Speciation Procedure

8.0 ICP-MS Quality Control

As required by EPA Method 200.8, Battelle's ICP-MS laboratory performed a quality control (QC) check, including an initial demonstration of laboratory capacity and periodic analyses of laboratory reagent blanks, fortified blanks, and calibration solutions as a continuing check on performance. A 5-point calibration was performed using certified As standard solutions with concentrations of 0.1, 5, 10, 30, and 50 µg/L. A linear calibration range of 0.1 to 50 µg/L was established with a correlation coefficient greater than 0.999. A method detection limit (MDL) was established to be 0.02 µg/L.

DI water and two source water samples including a groundwater and a surface water collected from two local water treatment plants were spiked with 10 µg/L of the As standard. A series of samples including QC samples (a calibration blank, calibration standards, quality control standards, and a laboratory fortified blank) were analyzed in a sequence shown in Table A-2. All percentage recoveries and relative percent difference (%RPD) values presented in Table A-2 are within the QC limits required by the Method 200.8.

Table A-2. ICP-MS Quality Control Check

Sample Sequence	Concentration	Percent Recovery	% RPD
Calibration Blank	+0.055		
Calibration Standard 2	4.94	99%	
Calibration Standard 4	29.0	97%	
Quality Control Standard	26.8		
Quality Control Standard	26.4		
Quality Control Standard	26.9		
Average	26.7	107%	0.9%
Laboratory Fortified Blank	8.07	101%	
DI Water (Laboratory Reagent Blank)	0.032		
DI Water Spiked with 10 µg/L As	9.56		
Ground Water	0.725		
Ground Water Spiked with 10 µg/L As	10.7		
Surface Water	1.19		
Surface Water Spiked with 10 µg/L As	9.80		
Quality Control Standard	63.7	106%	
Calibration Blank	-0.018		
Calibration Standard 2	5.22	104%	
Calibration Standard 4	28.9	96%	
Quality Control Standard	26.3	105%	
Laboratory Fortified Blank	7.92	99%	

9.0 Verification of Arsenic Speciation Method

Verification of the arsenic speciation method was performed in Battelle's laboratories using sodium arsenite (NaAsO_2) and disodium hydrogen arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) as As (III) and As (V) model compounds. The source water used in the ICP-MS QC check was also used in the verification study to more closely mimic field conditions.

DI water was spiked with 10 or 50 $\mu\text{g/L}$ of an As (III) or an As (V) standard solution.

Groundwater and surface water were spiked with 10 or 50 $\mu\text{g/L}$ of the As (V) standard. The pH of each solution was adjusted to 2, 3, or 4 using an ultra-pure sulfuric acid. Thereafter, the procedure described in Section 6.0 was followed. The samples before and after the resin column treatment were analyzed for total arsenic by ICP-MS.

The results show that the recoveries of As (III) from the resin columns ranged from 93.2 to 97.3%. The amount of As (V) retained in the resin columns ranged from 91.5 to 100%. The results also indicate that the difference in arsenic recovery/retention between the samples of pH 2 and the samples of pH 4 was less than 6%.

10.0 References

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